

## **REMARKS**

In the Office Action mailed on October 20, 2008, the previously made rejections of the claims under 35 U.S.C. §103(a) as unpatentable over Hampden-Smith et al. were withdrawn in light of arguments made in Amendment A. Claims 1, 2, 5-24 and 51 are rejected under §103(a) over Hampden-Smith in further view of U.S. Publication No. 2004/0045816 to Masel et. al. ("the Masel Publication"). Claims 3-4 are rejected as obvious under §103(a) over these two references in further view of 3,297,487 to Pomeroy. These rejections are traversed for the reasons set forth below.

### **A. INITIAL COMMENTS – TYPOGRAPHICAL ERRORS IN OFFICE ACTION**

Before addressing these rejections in detail, it is initially noted that the Office Action includes some significant typographical errors. For example, page 3 of the Office Action states "...with respect to claims 1 and 16, 100% formic acid may be used (par. 6)" (referring to Hampden-Smith) and page 4 states that "...Hampden-Smith teaches the same fuel ... as set forth by the applicant ...". Page 4 also states, however, that "Hampden-Smith does not disclose: formic acid fuel ... 25% to 65% formic acid fuel ...".

These citations are directly contradictory – some cite Hampden-Smith for disclosure of formic acid fuel while others admit that Hampden-Smith does not disclose formic acid fuel. Further, Hampden-Smith was cited as disclosing formic acid fuel in the March 31, 2008 Office Action, but those rejections were withdrawn in the current Action following Applicant's arguments in Amendment A regarding deficiencies in Hampden-Smith (specifically, that it did not teach formic acid fuels). The Masel publication is newly cited in the current Office Action for disclosure of a formic acid fuel solution. It also appears that the paragraphs on pages 3-4 of the current Office Action are identical to corresponding paragraphs from the March 31 Office Action.

On December 11, 2008, applicant's undersigned attorney discussed the above inconsistencies with the examiner on the phone. The examiner confirmed that Hampden-

Smith was not being cited as disclosing a formic acid fuel solution, that the Masel publication was, and that any citation to Hampden-Smith as disclosing a formic acid fuel solution in the current Office Action was an unintentional typographical error that resulted from the examiner mistakenly repeating paragraphs from the March 31 Office Action into the October Office Action. The merits of the rejections were not otherwise discussed during the call, and no agreements were reached.

The below remarks have been presented with the understanding that the Masel Publication is cited for disclosure of formic acid fuel solutions and Hampden-Smith is not. Should this not be the case clarification is required.

**B. THE MASEL PUBLICATION CANNOT BE A §103(A) REFERENCE**

The obviousness rejections of all claims has been made under §103(a) and cite the Masel Publication. The Masel Publication was published on March 11, 2004 and filed on September 11, 2002. The publication date is less than one month before the filing date of the present application (April 2, 2004). It is assumed that the Masel Publication is therefore being cited under §103 as a §102(a) prior art reference. An affidavit under 37 C.F.R. §1.131 is provided herewith that is effective to establish the invention of claims 1-24 and 51 on a date prior to the publication date of the Masel Publication. As a result of this Affidavit, the Masel Publication is no longer available as a §103 reference by way of §102(a).

It is further noted that the Masel Publication cannot be cited as a §103 reference by way of §102(e). 35 U.S.C. §103(c) precludes §102(e) references from being §103 prior art references if: “the subject matter (of the cited reference) and the claimed invention were, at the time the claimed invention was made, owned by the same person or subject to an assignment to the same person.” 35 U.S.C. §103(c). The subject matter of the Masel Publication and the corresponding presently rejected claims satisfy this condition – the presently claimed invention at the time of invention was subject to an assignment to The Board of Trustees of the University of Illinois. This is confirmed by the Assignment recorded in this matter on September 24, 2004 and recorded on reel/frame 015821/0361; and

by the assignment shown on the face of the Masel Publication and recorded on October 28, 2002 and recorded at reel/frame 013431/0474.

Because the Masel Publication cannot properly be cited as a §103 reference against the current claims, no prima facie obviousness case has been presented against any of the claims and the current rejections must be withdrawn.

No admission is made or shall be inferred by this traversal of the Masel Publication. Applicant does not admit any particular disclosure of the Masel Publication or any other cited reference or the relevance of those disclosures to the patentability of the present claims. Applicant expressly reserves the right to argue additional grounds of traversal regarding any cited reference in a future submission if necessary or appropriate.

### C. CONCLUSION

In conclusion, it is submitted that the claims in their present form are allowable. Timely examination and allowance are respectfully requested.

If a Petition under 37 C.F.R. §1.136(a) for an extension of time for response is required to make the attached response timely, it is hereby petitioned under 37 C.F.R. §1.136(a) for an extension of time for response in the above-identified application for the period required to make the attached response timely. The Commissioner is hereby authorized to charge fees which may be required to this application under 37 C.F.R. §§1.16-1.17, or credit any overpayment, to Deposit Account No. 07-2069.


Respectfully submitted,

GREER, BURNS & CRAIN, LTD.

February 6, 2009

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By

  
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Richard I. Masel et al.  
Serial No.: 10/817,361  
Conf. No.: 2569  
Filed: April 2, 2004  
For: IMPROVED PALLADIUM-BASED  
ELECTROCATALYSTS AND FUEL  
CELLS EMPLOYING SUCH  
ELECTROCATALYSTS  
Art Unit: 1795  
Examiner: Wills, Monique M.

Mail Stop Amendment  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**DECLARATION OF PRIOR INVENTION TO OVERCOME**  
**CITED PUBLICATION (37 C.F.R. §1.131)**

**PURPOSE OF DECLARATION**

This Declaration is to establish completion of the invention as claimed in at least claims 1-24 and 51 of this application in the United States at a date prior to March 11, 2004. The person making this Declaration is an inventor.

## DECLARATION


1. The invention as claimed in at least claims least claims 1-24 and 51 of this application was completed before March 11, 2004.

2. Exhibit A attached hereto is a copy of an invention disclosure prepared with my input and submitted on a date prior to March 11, 2004 to the patent attorneys that prepared and filed the present application. Portions of the document not relevant have been redacted.

3. During the period beginning before March 11, 2004 until the application was filed on April 2, 2004; preparation of a patent application was diligently pursued. During this period a patent attorney prepared a patent application, I discussed the invention as claimed by at least claims 1-24 and 51 with a patent attorney and reviewed at least one draft of the final patent application.

4. As a person signing below, I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or

imprisonment or both under 18 U.S.C. §1001, and that such willful statements may jeopardize the validity of this application or any patent issued thereon.

	Signature
Declarant's Signature:	 _____
	Richard I. Masel
Date:	<u>Jan 21, 2009</u>
Address:	<u>2603 Lakeview</u> <u>Champaign IL 61822</u> _____
Citizenship:	USA

# EXHIBIT A

# **INVENTION DISCLOSURE FORM**

**What is the technical field of the invention?**

This invention describes a new anode catalyst formulation for formic acid fuel cells that increases the current and voltage efficiency of the fuel cell.

(PORTION REDACTED)

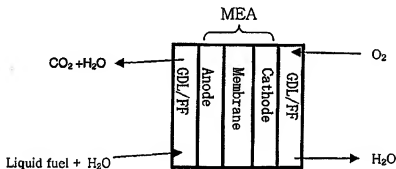


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Describe your solution here in 25 words or less.

A cheaper fuel cell anode catalyst, Pd black or supported Pd nano-particles, effectively enhances formic acid electro-oxidation through a path directly oxidized a fuel to CO<sub>2</sub> and hence avoids CO poisoning of catalyst.

Illustrate your solution using at least one drawing. In the case of a method, include process flow diagrams.



*Fuel cell membrane electrode assembly (MEA) and fuel cell reactions  
GDL: gas diffusion layer; FF: flow field*

Referring to each drawing, describe how your solution works.

In a fuel cell, chemical energy of reaction between fuel and oxidant is directly converted into electrical energy, producing current at a certain voltage. Catalysts promote the electrochemical reactions, i.e. fuel oxidation and oxidant reduction.

Membrane electrode assembly (MEA) is a key component in a fuel cell, which includes an anode electrode for the fuel oxidation reaction, a cathode electrode for the oxidant reduction reaction, and a polymer electrolyte membrane in between to provide an ionic conduction path. Typically a gas diffusion layer (GDL) is placed next to catalyst layer.

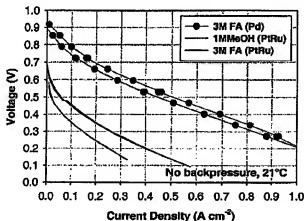
In a direct formic acid fuel cell (DFAFC), catalysts promote electrode reactions at the cathode and the anode. Platinum-ruthenium black are typical anode catalyst in a MEA for DFAFC or DMFC.

To Improve the fuel cell performance and energy efficiency, an anode catalyst is developed with palladium nanoparticles or the palladium nanoparticles supported on conductive carbon. The catalyst significantly promotes the anode electrode reaction and hence produces a performance much better than the widely accepted commercial anode catalyst Pt-Ru black.

**Describe the structural and/or functional differences between your solution and the prior solution(s).**

By using novel Pd nanoparticle catalysts, we are able to significantly reduce the costs of fuel cell systems since fuel cell performance with Pd anode catalyst is several times higher than that with the prior art catalyst PtRu. Moreover, Pd is cheaper than Pt. Pd also results in an increase in the fuel cell system voltage efficiency and avoids production of carbon monoxide, an intermediate, during formic acid oxidation (when compared to Pt, PtRu and related catalysts). This all translates into higher power density, higher energy efficiency, and lower fuel cell cost.

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*Figure 1 Polarization plots of formic acid (FA)/air or methanol (MeOH)/air fuel cell at 21°C. The flow rate of liquid fuel to the anode was 1 ml min<sup>-1</sup>. Air was supplied to the cathode at a flow rate of 350 ml min<sup>-1</sup> without any back-pressure and humidification. Anode catalysts are indicated in the legend.*

The new anode formulation used in this work was a composite containing a ~85 wt% Pd anode catalyst and recast Nafion™ ionomer. An in house developmental sample of the Pd nano-particle catalyst or Aldrich Pd nano-particle catalyst was used. The performance of the new composite material reported here has been compared to that of a commercial PtRu black catalyst (Johnson Matthey, UK). The cathode catalyst used was an unsupported Pt black catalyst (Johnson Matthey, UK). The anode and cathode catalyst inks were made by mixing appropriate amount of catalyst powders with 5% Nafion™ solution (1100 EW, Solution Technology, Inc., USA). The inks were applied to the Nafion™ 115 membrane, which was fixed on a vacuum table. Ink application was typically performed at 60°C, after which the membrane was thermally cured at 80°C for 15 minutes. The effective composition of unsupported anode catalyst was 85 wt% of Pd nano-particles or PtRu black and 15 wt% of recast Nafion™. The optimized cathode ink formulation was approximately 90 wt% Pt black and 10 wt% Nafion™. Cathode Pt loading 8 mg Pt cm<sup>-2</sup>; anode Pd or PtRu black loading 10 mg cm<sup>-2</sup>. The geometric surface area of all MEAs used in this work was 5 cm<sup>2</sup>.

Anode of MEAs was firstly cleaned up by cycling potential between 0.1 and 1.2 V. MEAs were conditioned in a fuel cell. Once no further change in cell performance and resistance was observed with time, the conditioning was ended. The formic acid fuel cell with Pd anode catalyst generated an extremely high performance using dry air at a room temperature of 21°C. The open circuit voltage was ca. 0.9 V. At 0.1 A cm<sup>-2</sup>, the cell voltage was above 0.75 V, which corresponds to a significantly high voltage efficiency of 54%. A maximum power density of ca. 270 mW cm<sup>-2</sup> was observed at 0.4 V (see Table 1). This is the best performance, according to our knowledge, for liquid feed fuel cell under the experimental conditions. Compared with the performance of fuel cells using well-accepted PtRu anode catalysts, Pd provides much better performance in all range of current density. DFAFC with Pd outperformed the one with PtRu more than 237% (or 3.4 times) in the maximum power density, and outperformed the DMFC with PtRu more than 440% (or 5.4 times). However, Pd is not a good anode catalyst for methanol oxidation.

**Table 1 Comparison of maximum power densities**

Fuel cells, 21°C	Maximum Power density mW cm <sup>-2</sup>
3M FA-air (Pd)	270
3M FA-air (PtRu)	80
1 M MeOH-air (PtRu)	50

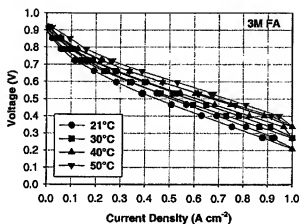


Figure 2. Polarization plots of (3 M) formic acid/air fuel cell at 21, 30, 40, and 50°C. The flow rate of liquid fuel to the anode was  $1 \text{ ml min}^{-1}$ . Air was supplied to the cathode at a flow rate of  $350 \text{ ml min}^{-1}$  without any back-pressure and humidification.

Figure 2 is polarization plot of the DFAFCs with 3.0M formic acid at different cell temperatures. At 50°C, current densities of 0.1, 0.5, and  $0.9 \text{ A cm}^{-2}$  are achieved at 0.82, 0.60, and 0.41V, respectively. Above  $1.0 \text{ A cm}^{-2}$ , the current density is beyond the safety limitation of our fuel cell test station (designed for small devices). Thus, the current density drop around  $1.0 \text{ A cm}^{-2}$  is not due to the mass transport of formic acid but programming safety protection. The DFAFCs can be well operated at different cell temperatures from 21 to 50°C. Above 50°C, there is no further performance benefit because of effects of partial pressure of oxygen, formic acid crossover, and temperature dependent kinetic. The maximum power densities are relatively encouraging at 40 and 50°C, 350 and  $375 \text{ mW cm}^{-2}$ , respectively. Even around ambient temperatures, the maximum power densities are 270 and  $300 \text{ mW cm}^{-2}$  at 21 and 30°C, respectively (see Table 2).

**Table 2 Power density of DFAFCs at different temperatures**

Temperature, °C	Power density @ 0.4V, $\text{mW cm}^{-2}$
21	270
30	300
40	350
50	375

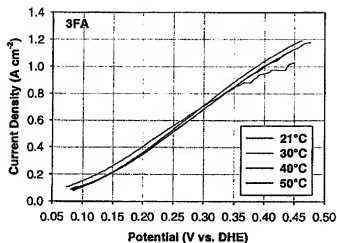


Figure 3 Anode polarization plots of 3.0 M formic acid at 21, 30, 40, and 50°C. The flow rate of formic acid to the anode was 1 ml min<sup>-1</sup>. Hydrogen was supplied to the cathode at a flow rate of 100 ml min<sup>-1</sup>.

Anode polarization plots of 3.0 M formic acid, as shown in Figure 3, indicate that the oxidation of 3.0 M formic acid at Pd anode is almost independent on cell temperatures used. At a low potential (e.g. 0.2 V), the anode polarization current density is as high as ca. 0.4 A cm<sup>-2</sup>. The onset potential for formic acid is lower than 0.07 V, our starting point. These results imply that the formic acid oxidation at Pd anode may have a very low activation energy. Therefore, the rate constant for formic acid oxidation is approximately temperature independent. This is also an evidence of that formic acid oxidation at Pd anode does not obeyed bi-functional mechanism, which refers to that sluggish oxidation of the intermediate species CO will be facilitated by oxygen-containing species generated at catalyst/electrode surface. The reaction rate constant is clearly temperature dependent as the sluggish CO oxidation has a high activation energy. A decomposition route of formic acid is not related to CO intermediate, and may not need any help from adsorbed oxygen-containing species. Pd nano-particles facilitate the decomposition of formic acid and hence results in a low activation energy. Therefore, increasing the temperature does not further favor its decomposition. Reasonably, the fuel cell polarization benefit (in Figure 2) with increasing temperature may come from cathode side, i.e. temperature dependent oxygen reduction.

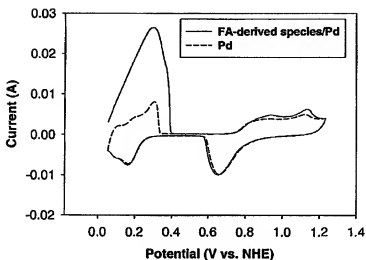


Figure 4 CVs of Pd nano-particles electrode in 0.5 M  $\text{H}_2\text{SO}_4$ . Potential scan rate is  $20 \text{ mV s}^{-1}$ . Dash line: clean Pd electrode; solid line: adsorbed species on Pd electrode, which was derived from formic acid (FA) oxidation.

In order to confirm that formic acid oxidation is via the direct decomposition route, rather than CO intermediate route, a conventional three-electrode electrochemical cell was used, with a Pd nano-particles becoming working electrode, a Pt wire acting as counter electrode and a silver/silver chloride reference electrode (but final potential is referred to normal hydrogen electrode, NHE). The Pd working electrode potential was then cyclically swept from 0.6 to 0.1 V in 3.0 M formic acid solution at a low scan rate of  $2 \text{ mV s}^{-1}$ . After the potential sweep, the Pd electrode was rinsed with  $\text{N}_2$  purged Milli-Q water to remove any un-reacted formic acid, and then transferred to another electrochemical cell with 0.5 M  $\text{H}_2\text{SO}_4$ , followed by the removal of chemisorbed species from the catalyst surface in a single voltammetric scan between 0.05 and 1.2 V at  $20 \text{ mV s}^{-1}$ . As demonstrated by plots in Figure 4 (solid line), a very big catalytic oxidation peak was observed with the peak potential at 0.3 V. There was no CO oxidation peak observed at potentials around 0.6 ~ 1.0 V, which are the potential range for CO oxidation at various metal electrodes, such as Pt, Au, Pd, Ag, and PtRu. The peak around 0.3 V definitely results from the adsorbed species on the Pd electrode because the Pd electrode surface was completely cleaned up at the potential beyond 0.4 V, which may be confirmed by comparing the cyclic voltammogram with the one of the clean Pd nano-particles electrode (dash line). We do not have further evidence about what kind of species or compound(s) the adsorbed species is/are. However, formate anion may be a most likely candidate since it can be oxidized at a low potential like 0.3 V. At least, CO intermediate may be excluded.

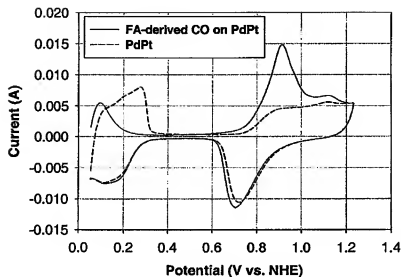
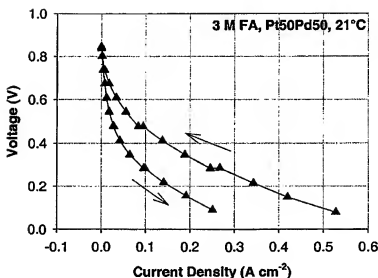


Figure 5 CVs of Pd50Pt50 nano-particles electrode in 0.5 M  $\text{H}_2\text{SO}_4$ . Potential scan rate is  $20 \text{ mV s}^{-1}$ . Dash line: clean Pd electrode; solid line: adsorbed species on Pd50Pt50 electrode, which was derived from formic acid oxidation.

When a Pt50Pd50 nano-particles electrode was used instead of Pd nano-particles electrode, the experiments were carried out in a way identical to Figure 4, as shown in Figure 5. A clear CO oxidation peak may be observed around 0.9 V (solid line). There was no catalytic oxidation peak around 0.3 V. The small peak at 0.1 V is a typical oxidation peak of adsorbed hydrogen atoms at electrode surface.

As CO intermediate species was formed during formic acid oxidation at Pd50Pt50, a bi-functional mechanism may be applied in this case, which is typical mechanism for formic acid oxidation or methanol oxidation at the prior art catalysts. Therefore, the fuel cell performance with Pd50Pt50 anode is comparable with the well-accepted PtRu anode catalyst, based on the same mechanism, as shown in Figure 6.



**Figure 6** Polarization plot of (3 M) formic acid/air fuel cell at 21°C. The flow rate of liquid fuel to the anode was 1 ml min<sup>-1</sup>. Air was supplied to the cathode at a flow rate of 350 ml min<sup>-1</sup> without any back-pressure and humidification.

Starting cell voltage at 0.1 V and getting up to 0.85 V, the cell generated a maximum power density of 70 mW cm<sup>-2</sup>. However, CO species was accumulated during the period and poisoned the catalyst, as well as ultimately led to a significant performance drop in the backward voltage change from 0.85 to 0.1 V. This is a typical example of effect of CO poisoning species on cell performance. Pd nano-particle catalyst may generate very high power output because there is no CO poisoning intermediate formed during formic acid oxidation at Pd anode.

**Table 3** Power density of DFAFCs with different concentrations of formic acid (FA)

[FA], M	Power density @ 0.4V, mW cm <sup>-2</sup>
3	270
10	200
15	150

Table 3 gives power density data of DFAFCs with different concentrations of formic acid, 3.0, 10.0, and 15.0 M, respectively. In general, low concentration of formic acid cannot sustain fuel cell operation at higher current densities because of mass transport limitation, e.g. 1.0 M formic acid. A use of high concentration of formic acid is helpful to overcome mass transport limitation. 3.0 M formic acid generates the largest maximum power densities, which is consistent with the results reported in our previous paper. The maximum power density decreases with changes in concentration from 3.0 to 15.0 M. However, the maximum power density of 150 mW cm<sup>-2</sup> can be achieved at 0.4 V with 15 M formic acid, which



still is a relatively high power density under the experimental conditions. The concentration-dependent crossover of formic acid may be one of crucial factors that affect the output of fuel cells. Another reason may be that formic acid exists in other form(s) under highly concentrated condition, e.g. dimers.

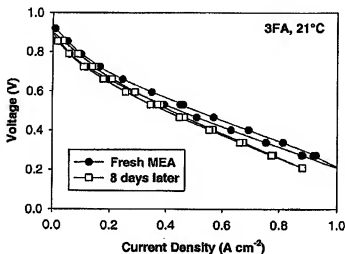


Figure 7 Polarization plots of (3 M) formic acid/air fuel cell at 21°C. The flow rate of liquid fuel to the anode was 1 ml min<sup>-1</sup>. Air was supplied to the cathode at a flow rate of 350 ml min<sup>-1</sup> without any back-pressure and humidification. The solid circle plot was obtained by using a fresh MEA with Pd anode; the empty square plot was observed by using the same MEA 8 days later.

In addition, the MEA with Pd anode has a good stability. For example, a newly prepared MEA with Pd anode generated a very good performance, as shown in Figure 7 (solid circle plot). Then the MEA was used for evaluation of temperature-dependence and concentration-dependence of the fuel cell performance. Eight days later, the MEA was tested again under the identical conditions. The result was represented by the empty square plot in Figure 7. There is no difference in the kinetic region of the cell polarization, below 0.2 A cm<sup>-2</sup>, which is an indication of the catalyst activity. A slight difference may be observed in the ohmic and mass transport polarization regions, which are affected by changes in polymer electrolyte membrane and recast polymer binder in the catalyst layers.

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